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Hydrodeoxygenation of Bio-polymer Precursors with Base Metal Catalysts

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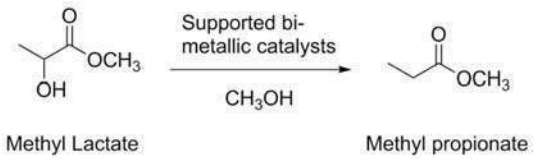
Future projections of declining and more expensive fossil reserves have stirred the chemical industry to find new pathways to convert biomass into renewable chemicals and fuels. The dominant storage form of carbon in nature is glucose accounting for 40-60 wt% of lignocellulosic biomass as cellulose. Industrial glucose processing involves its conversion to fructose, which is a key intermediate in reaction pathways towards furanic and carboxylic acid platform chemicals like, e.g. 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, lactic acid and levulinic acid [1].

Lactic acid (LA) is produced industrially in large scale from glucose by a fermentative process, however attractive, alternative chemo-catalytic processes based on Lewis acid zeolites are also emerging [2]. LA is an important feedstock to bio-degradable plastics, but can also serve as a feedstock for producing precursors (e.g. methyl propionate, MP) to existing acrylic plastics such as poly(methylmethacrylate) (PMMA). Currently, the preferred MP production route in industry is methoxycarbonylation of ethylene with carbon monoxide and methanol using a Pd-based homogeneous catalyst in a batch reactor despite major drawbacks such as, e.g. cautious handling of reactant as well as tedious catalyst recovery and recycling [3].

Here we report highly selective and efficient hydrodeoxygenation (HDO) of alkyl lactates to the corresponding alkyl propionates in alcohols with cheap and reusable base metal catalysts (Scheme 1). Under optimized reaction conditions an excellent yield of 77% MP was obtained from ML over Fe-Ni/ZrO_2 in methanol. Importantly, the introduced catalyst system proved generally applicable for HDO of compounds with α-hydroxyl groups, thereby making the system highly interesting for biomass valorization.



Scheme 1. HDO of ML to MP in methanol

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